FERROCHROME PRODUCTION

Jenny Lu

PURPOSE

- Ferrochrome is an alloy of Cr and Fe
  - Worldwide production in 2006 exceeded 28Mt
  - 80% used for the production of stainless steel
- Stainless steel is crucial in many applications
- Use FactSage to model production process
  - Direct current electric arc furnace

RAW MATERIALS

Chromite ore fines:

- 43% Cr_2O_3
- 22% FeO
- 16% MgO
- 13% Al_2O_3
- 6% SiO_2

Fluxes:

- Quartz = 100% SiO_2
- Limestone = 100% $CaCO_3$

Carbon source:

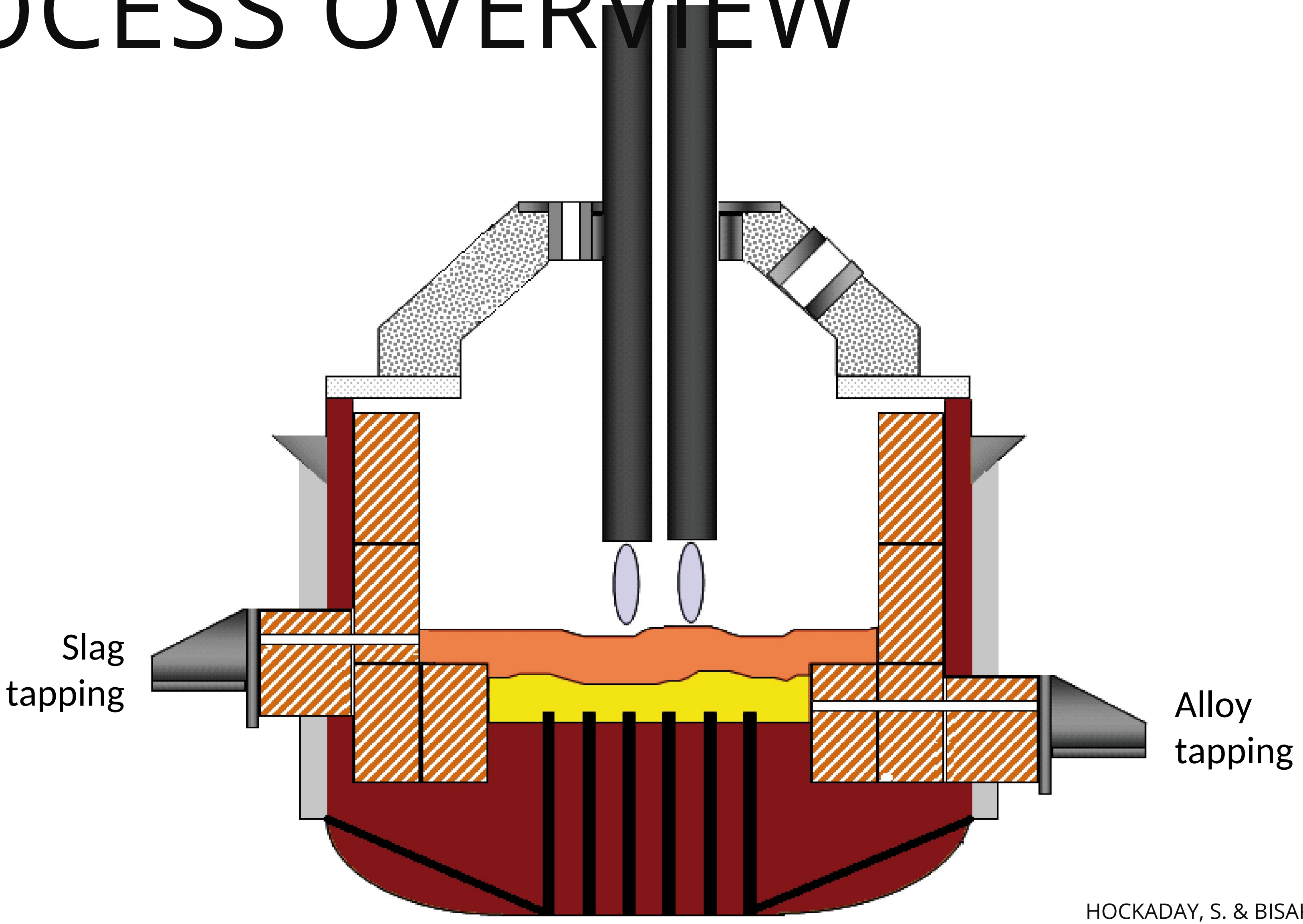
- Anthracite/coke = 100% C

PROCESS OVERVIEW

DC electric arc furnace

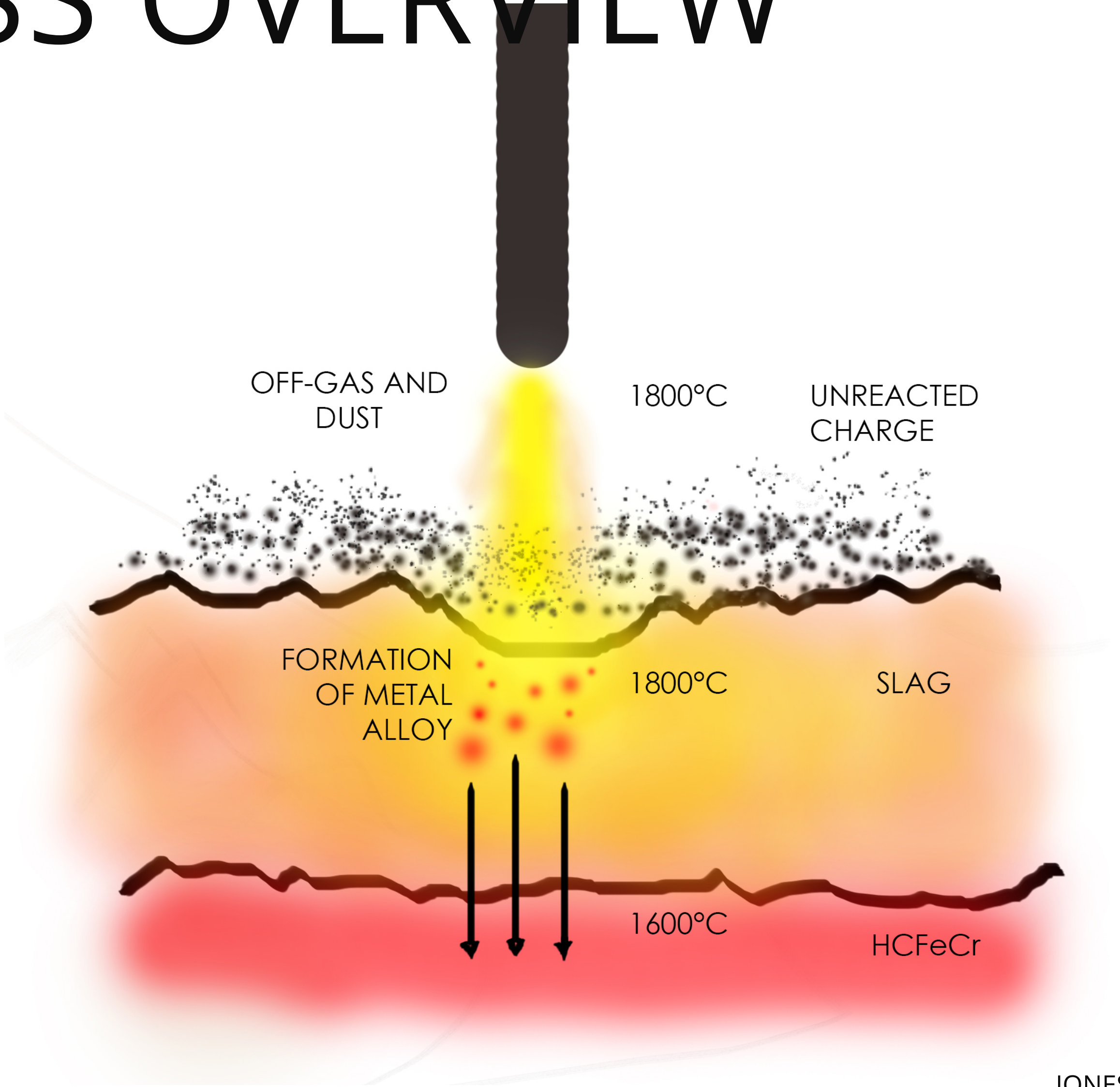
- Electrode is not submerged in melt
- Ore fines are used directly with no need for agglomeration
- Energy provided from electric arc from top electrode and bottom electrode

PROCESS OVERVIEW



HOCKADAY, S. & BISAKA, K. (2010)

PROCESS OVERVIEW



JONES, REYNOLDS, & CURR. (2011)

REACTION ZONE

Reduction of Cr_2O_3 (from ore) to create metallic Cr

- $Cr_2O_3 + 3C \rightarrow 2Cr + 3CO$

Reduction of FeO (from ore) to create metallic Fe

- $FeO + C \rightarrow Fe + CO$

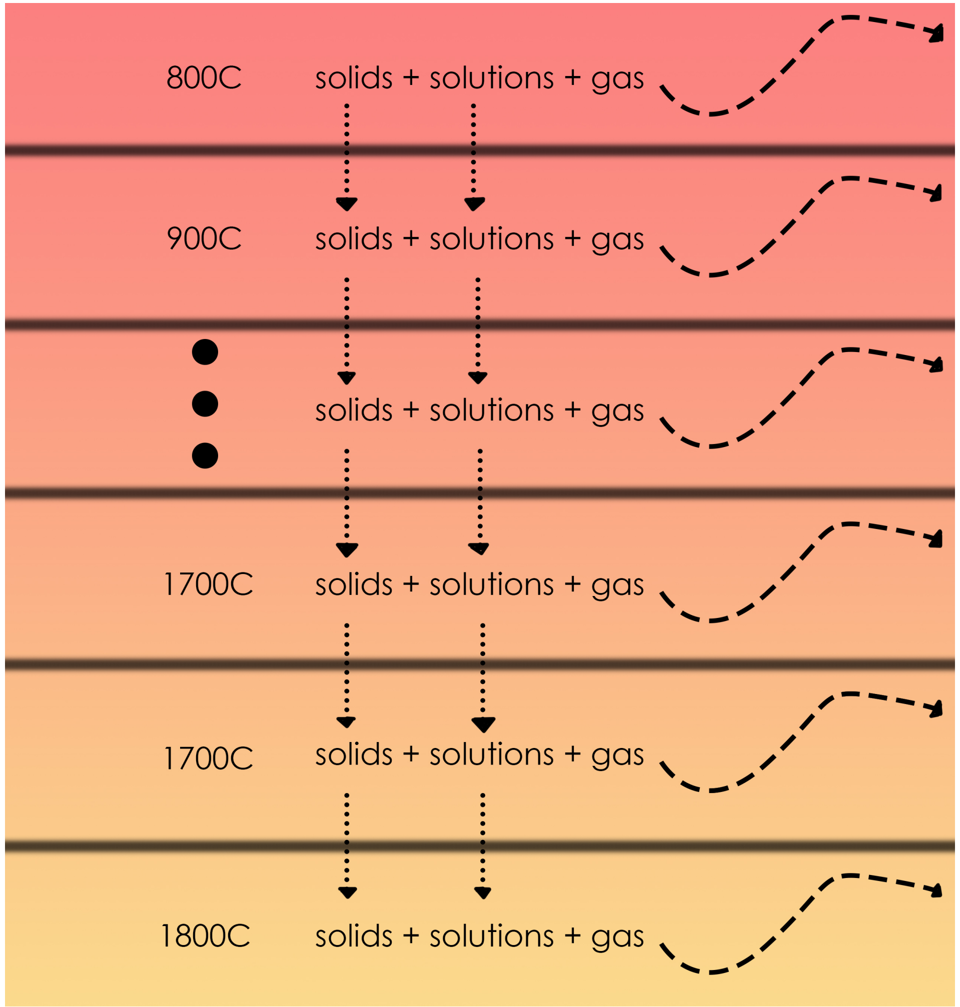
Thermal decomposition of $CaCO_3$ (from limestone) to create slag

- $CaCO_3 \rightarrow CaO + CO_2$

Minor reduction of SiO_2 (from quartz)

- $SiO_2 + 2C \rightarrow Si + 2CO$

FACTSAGE SIMULATION

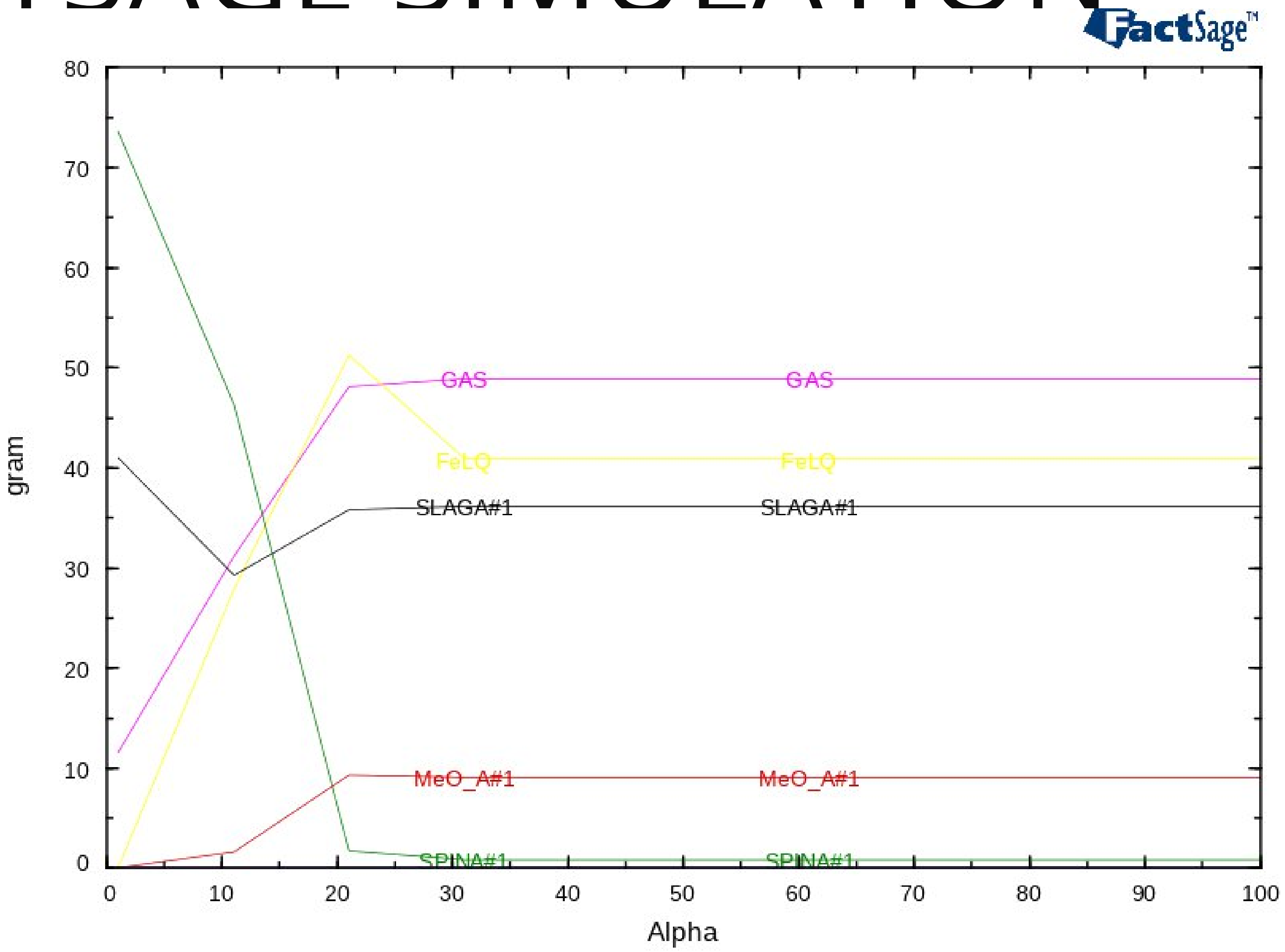


FACTSAGE SIMULATION

Additional cooling reaction for metal

�FeLQ phase @ 1800℃ � FeLQ phase @ 1600℃

FACTSAGE SIMULATION



FACTSAGE SIMULATION

- From FToxid the following were observed to form:
  - SLAGA – slag
  - SPINA – spinel
  - MeO_A – monoxide
  - cPyrA – clinopryoxene
  - Mel – mellite
  - OlivA – olivine

FACTSAGE SIMULATION

Phase selection

- Fe-LQ from FTmisc for final metal alloy (FeCr) phase
- All gases for formation of off-gas
- All pure solids for raw materials

FACTSAGE SIMULATION

Final amounts used:

- 100t chromite ore
- 18t anthracite (C)
- 11t limestone ($CaCO_3$)
- 7t quartz (SiO_2)

Ore composition (wt%)							
Cr_2O_3	FeO	MgO	Al_2O_3	SiO_2	Total (T)	Temperature (C)	Pressure (atm)
43	22	16	13	6	100	800	3
						50	
Quartz composition (wt%)							
SiO_2					Total (T)		
100					7	Slag tap (C)	
						1800	
Limestone composition (wt%)							
$CaCO_3$					Total (T)	Alloy tap (C)	
100					11	1600	
Anthracite composition (wt%)							
C					Total (T)		
100					18		
Ore amount (T)					Quartz amount (T)	Limestone amount (	Anthracite amount (T)
Cr_2O_3	FeO	MgO	Al_2O_3	SiO_2	SiO_2	$CaCO_3$	C
43	22	16	13	6	7	11	18
					READ THESE		

INITIAL RESULTS

Temp	GAS	FeLQ	SLAGA#1	SPINA#1	MeO_A#1	cPyrA#1	Mel_	OlivA#1
800	5.428147	0	0	80.06137	0	0.13893	18.1541	0
900	3.523896	0	0	76.49374	0	15.63641	5.23E+00	6.92E+00
1000	2.739676	0	0	71.84328	0	22.23049	0	0
1100	1.531072	0	0	66.55771	0	15.8678	0	0
1200	2.657246	20.19556	0	61.30763	0	16.54006	0	0
1300	17.42087	35.73447	14.28835	2.54E+01	0	0	4.50593	12.29421
1400	3.584228	40.66413	20.08562	17.17929	0	0	0	12.68443
1500	0.715724	47.02463	28.8185	13.5639	1.204037	0	0	5.10277
1600	0.427016	49.87108	35.32398	10.22222	2.554848	0	0	0
1700	0.336561	49.90378	37.76875	7.127817	2.835223	0	0	0
1800	0.453292	49.91694	43.71593	0.773364	2.776028	0	0	0

INITIAL RESULTS – ALLOY

Alloy (t)	Fe	Cr	Ca	Si	Al	Mg	O	C
50	34.5%	58.8%	0.0%	1.8%	0.0%	0.0%	0.0%	4.8%

- Cr/Fe ratio = 1.56

Plant data from Mintek pilot plant

	Cr%	Cr/Fe ratio	C%	Si%
Minimum	48	1.22	5.3	0.4
Maximum	72	4.08	9.8	7.3

INITIAL RESULTS – SLAG

Slag (t)	Al_2O_3	SiO_2	CaO	FeO	Fe_2O_3	MgO	CrO	Cr_2O3
42	28.3%	26.6%	14.8%	0.0%	0.0%	29.5%	0.7%	0%

- slag basicity ratio = $(CaO+MgO)/Al_2O_3$ = 1.56
- mass slag/mass alloy = 0.88

Plant data from Mintek pilot plant

	Al_2O_3%	SiO_2%	MgO%	CaO%
Minimum	30	20	20	10
Maximum	40	30	30	15

HOCKADAY, S. & BISAKA, K. (2010)

EFFECT OF INCREASING C – ALLOY

Alloy (t)	Fe	Cr	Ca	Si	Al	Mg	O	C
55	30.9%	53.1%	0.0%	8.9%	0.5%	0.1%	0.0%	6.4%

- Cr/Fe ratio = 1.72

Plant data from Mintek pilot plant

	Cr%	Cr/Fe ratio	C%	Si%
Minimum	48	1.22	5.3	0.4
Maximum	72	4.08	9.8	7.3

EFFECT OF INCREASING C – SLAG

Slag (t)	Al_2O_3	SiO_2	CaO	FeO	Fe_2O_3	MgO	CrO	Cr_2O3
27	45.6%	8.7%	22.7%	0.0%	0.0%	23.0%	0.0%	0%

- slag basicity ratio = $(CaO+MgO)/Al_2O_3$ = 1.00
- mass slag/mass alloy = 0.49

Plant data from Mintek pilot plant

	Al_2O_3%	SiO_2%	MgO%	CaO%
Minimum	30	20	20	10
Maximum	40	30	30	15

HOCKADAY, S. & BISAKA, K. (2010)

EFFECT OF DECREASING SI – ALLOY

Alloy (t)	Fe	Cr	Ca	Si	Al	Mg	O	C
50	30.9%	53.1%	0.0%	8.9%	0.0.%	0.0%	0.0%	5.0%

- Cr/Fe ratio = 1.71

Plant data from Mintek pilot plant

	Cr%	Cr/Fe ratio	C%	Si%
Minimum	48	1.22	5.3	0.4
Maximum	72	4.08	9.8	7.3

EFFECT OF DECREASING SI – SLAG

Slag (t)	Al_2O_3	SiO_2	CaO	FeO	Fe_2O_3	MgO	CrO	Cr_2O3
34	30.6%	24.0%	18.0%	0.0%	0.0%	26.9%	0.6%	0%

- slag basicity ratio = $(CaO+MgO)/Al_2O_3$ = 1.47
- mass slag/mass alloy = 0.69

Plant data from Mintek pilot plant

	Al_2O_3%	SiO_2%	MgO%	CaO%
Minimum	30	20	20	10
Maximum	40	30	30	15

HOCKADAY, S. & BISAKA, K. (2010)

EFFECT OF REACTION WITH SLAG

Introduce additional reaction between metal and slag

EFFECT OF SLAG REACTION – ALLOY

Alloy (t)	Fe	Cr	Ca	Si	Al	Mg	O	C
54	31.8%	54.3%	0.8%	2.6%	1.2%	1.4%	3.4%	4.4%

- Cr/Fe ratio = 1.71

Plant data from Mintek pilot plant

	Cr%	Cr/Fe ratio	C%	Si%
Minimum	48	1.22	5.3	0.4
Maximum	72	4.08	9.8	7.3

EFFECT OF SLAG REACTION – SLAG

Slag (t)	Al_2O_3	SiO_2	CaO	FeO	Fe_2O_3	MgO	CrO	Cr_2O3
42	28.3%	26.6%	14.8%	0.0%	0.0%	29.5%	0.7%	0%

- slag basicity ratio = $(CaO+MgO)/Al_2O_3$ = 1.56
- mass slag/mass alloy = 0.77

Plant data from Mintek pilot plant

	Al_2O_3%	SiO_2%	MgO%	CaO%
Minimum	30	20	20	10
Maximum	40	30	30	15

HOCKADAY, S. & BISAKA, K. (2010)

EFFECT OF INCREASING PRESSURE

Furnace is operated below 1atm in reality, however simulation done at 3atm

From Le Chatelier's Principle, increasing pressure suppresses CO formation

- CO gas bubble formation requires nucleation of bubble
- Surface energy required to form new surface must be overcome
- Typically this is an endothermic reaction
- Large kinetic driving force may be required

FINAL RESULTS

Temp	GAS	FeLQ	SLAGA#1	SPINA#1	MeO_A#1	cPyrA#1	Mel_	OlivA#1
800	5.428147	0	0	80.06137	0	0.13893	18.1541	0
900	3.523896	0	0	76.49374	0	15.63641	5.23E+00	6.92E+00
1000	2.739676	0	0	71.84328	0	22.23049	0	0
1100	1.531072	0	0	66.55771	0	15.8678	0	0
1200	2.657246	20.19556	0	61.30763	0	16.54006	0	0
1300	17.42087	35.73447	14.28835	2.54E+01	0	0	4.50593	12.29421
1400	3.584228	40.66413	20.08562	17.17929	0	0	0	12.68443
1500	0.715724	47.02463	28.8185	13.5639	1.204037	0	0	5.10277
1600	0.427016	49.87108	35.32398	10.22222	2.554848	0	0	0
1700	0.336561	49.90378	37.76875	7.127817	2.835223	0	0	0
1800	0.453292	49.91694	43.71593	0.773364	2.776028	0	0	0

FINAL RESULTS – ALLOY

Alloy (t)	Fe	Cr	Ca	Si	Al	Mg	O	C
50	34.2%	58.5%	0.0%	1.1%	0.0%	0.0%	0.0%	6.1%

- Cr/Fe ratio = 1.56

Plant data from Mintek pilot plant

	Cr%	Cr/Fe ratio	C%	Si%
Minimum	48	1.22	5.3	0.4
Maximum	72	4.08	9.8	7.3

FINAL RESULTS – SLAG

Slag (t)	Al_2O_3	SiO_2	CaO	FeO	Fe_2O_3	MgO	CrO	Cr_2O3
44	28.0%	27.1%	14.1%	0.0%	0.0%	30.2%	0.5%	0%

- slag basicity ratio = $(CaO+MgO)/Al_2O_3$ = 1.56
- mass slag/mass alloy = 0.88

Plant data from Mintek pilot plant

	Al_2O_3%	SiO_2%	MgO%	CaO%
Minimum	30	20	20	10
Maximum	40	30	30	15

HOCKADAY, S. & BISAKA, K. (2010)

DISCUSSION

In general the level of carbon in alloy is controlled by equilibrium between Si and C when smelting is carried out above stoichiometric requirement

- Mechanism is complex and still not well understood

HOCKADAY, S. & BISAKA, K. (2010)

DISCUSSION

Unlike submerged-arc furnace where the metal from the smelting reactions is subjected to refining as the droplets filter through the viscous chromium oxide-rich slag above the alloy; it is believed that most of the refining in the open-bath furnace could be happening at the interface between metal and slag.

This does not permit refining reactions to proceed to any significant extent as the reactions are limited by:

- Surface area
- Residence time
- Temperature

MUKHERJEE. (2010)

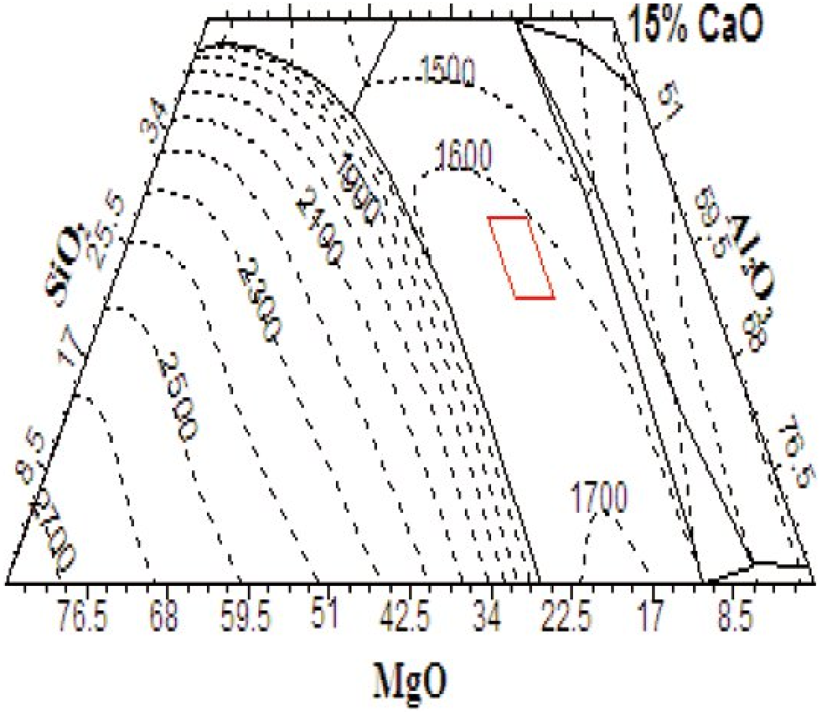
DISCUSSION

Presence of spinel and monoxide

- Spinel (0.7t)
  - 53 wt.% $MgAl_2O_4$
  - 29 wt.% Al_3O_4
  - 11 wt.% Mg_3O_4[2-]
  - 6 wt.% $AlMg_2O_4$[1-]
  - 1 wt.% $MgCr_2O_4$
- Monoxide (2.8t)
  - 92 wt.% MgO
  - 7 wt.% Al_2O_3
  - 1 wt.% Cr_2O_3

DISCUSSION

Un-fluxed slags produced from reduction of iron and chromium oxides have liquidus temperatures exceeding 1900°C



HOCKADAY, S. & BISAKA, K. (2010)

DISCUSSION

Differences arise from variations in ore composition

	MgO%	Al_2O_3%	SiO_2%	CaO%	Cr_2O_3%	FeO%	Cr/Fe
Minimum	9.4	6.5	0.6	0.1	42.2	11.9	1.3
Maximum	20.5	16.9	6.9	0.3	53.8	27.3	3.8

Full compositional analysis not available – percentage of ore not composed of compounds given above

HOCKADAY, S. & BISAKA, K. (2010)

DISCUSSION

Ore composition used contains too much MgO and Al2O3

Using:

- 43% Cr
- 22% Fe
- 12% MgO
- 11% Al_2O_3
- 6% SiO_2

Monoxide and spinel at 1800°C (±~100°C) eliminated

DISCUSSION

Temp	GAS	FeLQ	SLAGA#1	SPINA#1	MeO_A#1	cPyrA#1	Mel_	OlivA#1
800	5.38435	0	0	78.00572	0	12.46102	9.509631	0
900	3.107144	0	0	74.37959	0	24.54615	0.00E+00	5.93E-01
1000	2.820236	0	0	65.19466	0	14.18726	0	0
1100	1.420496	0	0	60.34038	0	8.378833	0	0
1200	4.176893	21.47241	0	52.09788	0	8.857605	0	0
1300	18.16619	35.73261	23.14109	1.70E+01	0	0	0	7.13889
1400	2.081839	42.77903	26.13363	11.59698	0	0	0	5.789434
1500	0.570458	48.04092	33.14409	9.052384	0	0	0	0.323524
1600	0.338787	49.86873	35.03426	7.030625	0	0	0	0
1700	0.326707	49.89923	37.49071	4.216965	0	0	0	0
1800	0.47626	49.91546	41.21519	0	0	0	0	0

FINAL RESULTS – ALLOY

Alloy (t)	Fe	Cr	Ca	Si	Al	Mg	O	C
50	34.2%	58.6%	0.0%	1.1%	0.0%	0.0%	0.0%	6.0%

- Cr/Fe ratio = 1.71

Plant data from Mintek pilot plant

	Cr%	Cr/Fe ratio	C%	Si%
Minimum	48	1.22	5.3	0.4
Maximum	72	4.08	9.8	7.3

FINAL RESULTS – SLAG

Slag (t)	Al_2O_3	SiO_2	CaO	FeO	Fe_2O_3	MgO	CrO	Cr_2O3
41	26.6%	28.7%	15.0%	0.0%	0.0%	29.1%	0.6%	0%

- slag basicity ratio = $(CaO+MgO)/Al_2O_3$ = 1.65
- mass slag/mass alloy = 0.83

Plant data from Mintek pilot plant

	Al_2O_3%	SiO_2%	MgO%	CaO%
Minimum	30	20	20	10
Maximum	40	30	30	15

HOCKADAY, S. & BISAKA, K. (2010)

SUMMARY

Overall, able to accurately model ferrochrome production process

Many factors neglected:

- Furnace size and geometry
- Impact of reductant used
- Feeding configuration
- Arc characteristics
- Furnace hydrodynamics
- etc.

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